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Electrochemical Thiophosphorylation of Olefins

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Abstract

The electrochemical oxidation of dialkyl hydrogen thiophosphites or their sodium and lithium salts in the presence of olefins proceeds through the stage of formation at the anode of a dialkylthiophosphoryl radical (RO)2PS, attachment of which to the alkene double bond yields the corresponding (RO)2P(S)/-R′ radical adduct. The further conversions of this adduct can take two routes. The first route involves abstraction of hydrogen atom from the dialkyl hydrogen thiophosphite, which is present in the reaction mixture, or from the solvent (MeCN) to form a saturated alkyl(cycloalkyl)thiophosphonate. By the second route, the adduct is oxidized at the anode to give a (RO)2P(S)/-+R′ carbocation, which forms an unsaturated 2-alkeneyl--2-cycloalkeneyl)thiophosphonate upon deprotonation. It is proposed that the predominance of one or the other of the reaction routes is determined by the competitive adsorption at the anode of starting and intermediate compounds, mainly the olefin and the radical adduct.